

Consideration of Long and Middle Range Interaction on the Calculation of Activities for Binary Polymer Solutions

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Abstract: We established a thermodynamic framework of group contribution method based on modified double lattice (MDL) model. The proposed model included the long-range interaction contribution caused by the Coulomb electrostatic forces, the middle-range interaction contribution from the indirect effects of the charge interactions and the short-range interaction from modified double lattice model. The group contribution method explained the combinatorial energy contribution responsible for the revised Flory-Huggins entropy of mixing, the van der Waals energy contribution from dispersion, the polar force, and the specific energy contribution from hydrogen bonding. We showed the solvent activities of various polymer solution systems in comparison with theoretical predictions based on experimental data. The proposed model gave a very good agreement with the experimental data.

Keywords: modified double lattice model, group contribution method, charge interaction, long range interaction, middle range interaction.

Introduction

For engineering purposes, it is often necessary to make estimate of activity for mixtures where only fragmentary data, or no data at all, are available. For vapor-liquid equilibria, such estimates can be made using a group-contribution method.¹

Since activity coefficients calculation using group-contributions was suggested by Langmuir,² the most widely used and best known of group-contribution method is the UNIFAC.³ The acronym UNIFAC denotes the UNIQUAC⁴ functional group activity coefficient. The UNIFAC correlation is based on a semi-empirical model for liquid polymer solutions called UNIQUAC (universal quasi-chemical activity coefficient). When compared with the experimental data, however, the UNIFAC equation shows deviations too large to satisfactorily explain the polymer solutions.

Oishi and Prausnitz⁵ modified the UNIFAC model by providing a free volume contribution suggested by Prigogine-Flory-Patterson theory for polymer solutions to consider the compressibility and change in density upon isothermal mixing.

Later, many modifications of UNIFAC model are reported by Holten-Andersen and Fredenslund,^{6,7} Chen *et al.*,⁸ Elbro

et al.,⁹ Kontogeogis *et al.*,¹⁰ and Bogdanic and Fredenslund.¹¹

Those methods are based on the UNIFAC correlation which is often successful for estimating phase equilibria in mixtures containing ordinary (nonpolymer) liquids.

The fundamental basis for existing group-contribution methods for polymer solutions is the lattice theory of Flory¹² and Huggins.¹³ To pursue a formal exact solution to the lattice model using advanced statistical and mathematical methods, Freed and coworkers^{14,15} developed a lattice-cluster theory for polymer-solvent system. This theory provides an exact mathematical solution for the Flory-Huggins model.

Hu *et al.*¹⁶ proposed a new theory called the double lattice model based on Freed's lattice-cluster theory and Bae *et al.*¹⁷ reported a modified double-lattice model and provided an exact mathematical form for the secondary lattice of the double lattice. Hu *et al.*¹⁸ presented the group contribution method including a revised Flory-Huggins entropy and a series expression for excess internal energy as well as a double lattice model to account for specific interactions.

Debye and Hückel¹⁹ presented the theory of inter-ionic attraction in aqueous electrolyte solutions. This theory first made it possible to calculate the ion activity coefficients at infinite dilution. In order to apply the Debye-Hückel theory

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to higher electrolyte concentrations, Stokes and Robinson²⁰ proposed the concept of ionic hydration, and derived a two parameter equation. Later several variations of the ionic hydration theory are reported: Glueckauf,²¹ Robinson *et al.*²² and Stokes and Robinson.²³ These theories are used for calculation of the activity of water in concentrated aqueous electrolyte solutions.

In the early 1970s, the integral techniques based on the Ornstein-Zernicke equation have been used to solve the primitive model of electrolyte solutions. Blum²⁴ used the method proposed by Baxter²⁵ for hard-sphere solutions and square-well potentials, and obtained a solution for the mean spherical approximation (MSA). Planche and Renon²⁶ generalized the model of Baxter by using the formalism of Blum, taking into account short-range forces between molecules in order to get a non-primitive representation of electrolyte solutions. Pitzer^{27,28} developed general equations for the thermodynamic properties of aqueous electrolytes based on the Debye-Hückel theory. However, if the Pitzer parameters are applied to the high concentration range (for example 10-20 M) very large deviations are obtained in most cases.

In last decades, numerous authors have modified the existing g^E model and EOS (Equation of State) model for non-electrolyte systems. Mock *et al.*²⁹ applied the NRTL model to electrolyte systems. Their model provides a consistent thermodynamic framework for the representation of the phase equilibrium of mixed solvent electrolyte systems. However, different parameters are required to calculate the VLE at different temperatures. Sander *et al.*³⁰ proposed an extended UNIQUAC model for mixed-solvent/electrolyte systems. Macedo *et al.*³¹ used a modified Debye-Hückel term derived from the McMillan-Mayer solution theory to replace the Debye-Hückel term in the Sander model.

The most widely used and best known of the g^E model for the electrolyte solution is LIQUAC.^{32,33} It consists of a Debye-Hückel term to account for long-range electrostatic interactions, the UNIQUAC equation for the description of short-range interactions among all particles, and a middle-range contribution to include all indirect effects of the charge interactions.

In this study, we propose a group-contribution model that can be used to describe solvent activities of polymer solutions and phase diagram of perfluorinated SPE/water system. The proposed model is based on a modified double lattice model, long range interaction and middle range interaction wherein the Helmholtz function of mixing includes the revised Flory-Huggins entropy contribution, the van der Waals energy contribution, and the specific energy contribution.

Model Development

Various types of interactions are taken into account for describing the activities of electrolyte and non-electrolyte

polymer solutions. In this study, we calculate the excess Gibbs energy as the sum of three contributions:

$$G^E = G_{LR}^E + G_{MR}^E + G_{SR}^E \quad (1)$$

G_{LR}^E represents the long-range (LR) interaction contribution caused by the Coulomb electrostatic forces, and mainly describes the direct effects of charge interactions.²⁸ G_{MR}^E represents the indirect effects of charge interactions. In order to distinguish the indirect effects from the non-charge short-range interactions of the non-electrolyte solution, and because some of the charge interactions (such as the charge-dipole interactions and charge-induced dipole interactions) are proportional to r^{-2} and r^{-4} , we shall refer to this term as the middle-range (MR) interaction contribution. (r is a distance with two particles).^{32,34} G_{SR}^E expresses the contribution of the non-charge interactions, which is identical to the short-range (SR) interactions in non-electrolyte solutions.

This model has two ways of usage according to the classification of non-electrolyte and electrolyte:

1. In case of non-electrolyte, only short range interaction is considered.
2. In case of electrolyte, short, mid, and long range are considered.

Long-Range Interaction Contribution. The long-range electrostatic interaction explained interaction between ion-ion. It gives rise to the Debye-Hückel limiting law, which states that the logarithm to the ionic activity coefficient at high dilution is proportional to the square-root of the ionic strength. In all the models presented in the literature, this contribution has been described by some or other form of the Debye-Hückel theory.

In this study, G_{LR}^E is calculated in terms of the Debye-Hückel theory as modified by Fowler and Guggenheim³⁴:

$$G_{LR}^E = -(3D)^{-1} \sum_{i=1}^{ion} s_i z_i^2 e^2 \tau(\kappa a) \quad (2)$$

where s_i is the number of i ions in the system, D is the solvent dielectric constant, a is the distance of closest approach between two ions and $\tau(x)$ is defined as

$$\tau(x) = 3x^{-3} \left[\ln(1+x) - x + \frac{x^2}{2} \right] \quad (3)$$

where $x = \kappa a$ and κ is the inverse of the shielding length commonly called Debye length which is a characteristic distance of interaction.

The expression for the long-range interaction contribution to the activity coefficients of solvent, s , follows the appropriate derivations of eq. (2). We assume the partial molar volume of the solvent s in the solution is approximated as the molar volume of the pure solvent.

$$\ln \gamma_s^{LR} = \left[\frac{2AM_s}{b^3} \right] \left[1 + bI^{1/2} - \frac{1}{1 + bI^{1/2}} - 2 \ln(1 + bI^{1/2}) \right] \quad (4)$$

where M_s is the molecular weight of the solvent s , I is an ionic strength and A and b are Debye-Hückel parameters.

$$I = 0.5 \sum_i m_i z_i^2 \quad (5)$$

$$A = 1.327757 \times 10^5 \frac{d^{0.5}}{(DT)^{1.5}} \quad (6)$$

$$b = 6.359696 \frac{d^{0.5}}{(DT)^{0.5}} \quad (7)$$

where T is the absolute temperature in Kelvin and D is the dielectric constant for a solvent. m_i is the molality of species i and d is the solvent molar density. These parameters are based on a value of 4 Å for the distance of closet approach.

Middle-Range Interaction Contribution. The G_{MR}^E term is the contribution of the indirect effects of charge interactions to the excess Gibbs energy. For a solution containing n_n moles of solvent n ($n=1, 2, \dots$, sol) and n_j moles of ion j ($j=1, 2, \dots$, ion), G_{MR}^E is obtained from the following equation:

$$\frac{G_{MR}^E}{RT} = \sum_k \sum_l B_{kl} x_k x_l \quad (8)$$

where B_{kl} is the interaction coefficient between species k and l (ion or molecule) and x_k and x_l are mole fractions of species k and l , respectively.

By using the simplest potential model for electrolyte solutions and from radial distribution theories of statistical thermodynamics, one can obtain an expression for the dependence of the indirect effect on the ionic strength. It seems reasonable to assume that B_{kl} , which represents all indirect effects caused by the charges, can be described by the following simple equation:

$$B_{ij}(I) = b_{ij} + c_{ij} \exp(a_1 I^{1/2} + a_2 I) \quad (9)$$

where b_{ij} and c_{ij} are middle-range interaction parameters between species i and j ($b_{ij} = b_{ji}$, $c_{ij} = c_{ji}$). a_1 and a_2 are constants which are determined empirically using a number of experimental data for electrolyte/solvent systems.³² These are estimated by fitting experimental polymer sorption VLE (Vapor-Liquid Equilibria) data of perfluoro-sulfonated polymer electrolyte membranes/water.³⁵

$$B_{ion,ion} = b_{ion,ion} + c_{ion,ion} \exp(-I^{1/2} + 0.13I) \quad (10)$$

$$B_{ion,solvent} = b_{ion,solvent} + c_{ion,solvent} \exp(-1.2I^{1/2} + 0.13I) \quad (11)$$

We assume that there are no middle-range interactions between solvents, so that eq. (8) can be simplified to

$$\frac{G_s^{MR}}{RT} = \sum_{sol, ion} B_{sol, ion}(I) x_{sol} x_{ion} + \sum_c \sum_a B_{ca}(I) x_c x_a \quad (12)$$

where c indices cover all cations and a indices cover all

anions.

By differentiating eq. (12) with respect to the number of moles of solvent and ions, one obtains

$$\begin{aligned} \ln \gamma_s^{MR} &= \sum_{ion} B_{s, ion}(I) x_{ion} - (M_s/M_m) \\ &\quad \sum_{sol, ion} [B_{sol, ion}(I) + IB'_{sol, ion}(I)] x'_{sol} m_{ion} \\ &\quad - M_s \sum_c \sum_a [B_{ca}(I) + IB'_{ca}(I)] m_c m_a \end{aligned} \quad (13)$$

Where x'_{sol} is the salt-free mole fraction of solvent sol, $B'(I)$ is equal to $B'(I) = dB(I)/dI$ and M_m is the mean molecular weight of mixed solvent (kg/mol) m and is calculated as

$$M_m = \sum x'_{sol} M_{sol} \quad (14)$$

Short-Range Interaction Contribution. The mostly existing model to describe the phase equilibria of non-electrolyte solution is UNIQUAC model.³ However, it gives a good representation only for such as hydrocarbons, ketones, esters and water, etc. In this study, we employ the modified double lattice model¹⁸ including group contribution method to take into account the van der Waals energy contribution, polar force and the specific energy contribution.

MDL Model.

Primary Lattice: Oh *et al.*¹⁸ proposed a new Helmholtz energy of mixing as the form of Flory-Huggins theory. The expression is given by

$$\frac{\Delta A}{N_r kT} = \left(\frac{\phi_1}{r_1}\right) \ln \phi_1 + \left(\frac{\phi_2}{r_2}\right) \ln \phi_2 + \chi_{OB} \phi_1 \phi_2 \quad (15)$$

where N_r is the total number of lattice sites and k is the Boltzmann's constant. r_i is the number of segments per molecule i . χ_{OB} is a new interaction parameter and function of r_i , $\tilde{\varepsilon}$:

$$\chi_{OB} = C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\varepsilon} - \left(\frac{1}{r_2} - \frac{1}{r_1} + C_\gamma \tilde{\varepsilon}\right) \tilde{\varepsilon} \phi_2 + C_\gamma \tilde{\varepsilon}^2 \phi_2^2 \quad (16)$$

$\tilde{\varepsilon}$ is a reduced interaction parameter given by

$$\tilde{\varepsilon} = \varepsilon/kT = (\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12})/kT \quad (17)$$

where ε_{11} , ε_{22} and ε_{12} are for the corresponding nearest-neighbor segment-segment interactions. Parameters, C_β and C_γ , are universal constants. These constants are not adjustable parameters and are determined by comparing with Madden *et al.*'s Monte-Carlo simulation data ($r_1=1$ and $r_2=100$). The best fitting values of C_β and C_γ are 0.1415 and 1.7985, respectively.¹⁸

Secondary Lattice: In Freed's theory,^{14,15} the solution of the Helmholtz energy of mixing for the Ising model is given by

$$\frac{\Delta A}{N_r kT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{z \tilde{\varepsilon} x_1 x_2}{2} - \frac{z \tilde{\varepsilon}^2 x_1^2 x_2^2}{2} + \dots \quad (18)$$

where, z is the coordination number and x_i is the mole fraction of the component i .

To obtain an analytical expression for the secondary lattice, we defined a new Helmholtz energy of mixing as the fractional form to improve the mathematical approximation defect by revising eq. (18). This secondary lattice is introduced as a perturbation to account for the oriented interaction. The expression is given by

$$\frac{\Delta A_{sec,ij}}{N_{ij}kT} = \frac{2}{z} \left[\eta \ln \eta + (1-\eta) \ln(1-\eta) + \frac{zC_\alpha \delta \tilde{\varepsilon}_{ij} (1-\eta) \eta}{1 + C_\alpha \delta \tilde{\varepsilon}_{ij} (1-\eta) \eta} \right] \quad (19)$$

where, $\Delta A_{sec,ij}$ is the Helmholtz energy of mixing of the secondary lattice for i - j segment-segment pair and N_{ij} is the number of i - j pairs, $\delta \tilde{\varepsilon}$ is the reduced energy parameter contributed by the oriented interactions and η is the surface fraction permitting oriented interactions. For simplicity, η is arbitrarily set to 0.3 as Hu *et al.*,¹⁶ suggested. C_α also is not an adjustable parameter and is determined by comparing with Panagiotopoulos *et al.*'s³⁶ Gibbs-Ensemble Monte-Carlo simulation data of Ising lattice. The best fitting value of C_α is 0.4880.¹⁸

Incorporation of Secondary Lattice Into Primary Lattice: To incorporate a secondary lattice, we replace ε_{ij} by $\varepsilon_{ij}^* - \Delta A_{sec,ij}/N_{ij}$ in eq. (17). If oriented interaction occurs in the i - j segment - segment pairs, we replace $\tilde{\varepsilon}$ by $\varepsilon^*/kT + 2\Delta A_{sec,ij}/N_{ij}kT$ in eq. (18). If oriented interaction occurs in the i - i segment - segment pairs, we replace $\tilde{\varepsilon}$ by $\varepsilon^*/kT - \Delta A_{sec,ii}/N_{ii}kT$. In this study, we assume the oriented interaction occurs in the i - i , j - j and i - j segment-segment pairs. We replace $\tilde{\varepsilon}$ by

$$\tilde{\varepsilon} = (\varepsilon_{11}^* + \varepsilon_{22}^* - 2\varepsilon_{12}^*) + \left(-\frac{\Delta A_{sec,11}}{N_{11}} - \frac{\Delta A_{sec,22}}{N_{22}} + \frac{2\Delta A_{sec,12}}{N_{12}} \right) \quad (20)$$

where ε_{11}^* , ε_{22}^* and ε_{12}^* are van der Waals energy interaction parameters. $\Delta A_{sec,11}$, $\Delta A_{sec,22}$ and $\Delta A_{sec,12}$ are the additional Helmholtz functions for the corresponding secondary lattice. If the oriented interaction in i - i , j - j segment-segment pairs is very smaller than interaction in i - j segment-segment pair, we can neglect interaction in i - i , j - j segment-segment pairs. And then eq. (20) becomes

$$\tilde{\varepsilon} = (-2\varepsilon_{12}^*) + \left(\frac{2\Delta A_{sec,12}}{N_{12}} \right) \quad (21)$$

To correlate MDL model to melting point depression theory, we require chemical potentials of components 1 and 2. The definition of chemical potential is

$$\frac{\Delta \mu_i}{kT} = \frac{\partial(\Delta A/kT)}{\partial N_i} \quad (22)$$

The final expression for the chemical potential can be written as

$$\begin{aligned} \frac{\Delta \mu_s^{SR}}{kT} &= \ln(1-\phi_2) - r_1 \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \phi_2 \\ &+ r_1 \left[C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon} \right] \phi_2^2 \\ &- 2r_1 \left[\left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + C_\gamma \tilde{\varepsilon} \right] \phi_2^3 + 3r_1 C_\gamma \tilde{\varepsilon} \phi_2^4 \quad (23) \end{aligned}$$

where ϕ_i is the segment fraction of component i , $\phi_i = N_i r_i / N_r$ and $N_r = \sum_m N_m r_m$ is the total number of segments in the system and r_i is the segment number of component s (salt).

The final equation of proposed model is presented by sum of eqs. (4), (13), and (23) and is written as

$$\begin{aligned} \frac{\Delta \mu_1}{kT} &= \left[\frac{2AM_s}{b^3} \right] \left[1 + bI^{1/2} - \frac{1}{1+bI^{1/2}} - 2\ln(1+bI^{1/2}) \right] + \ln x_s \\ &+ \sum_{ion} B_{s,ion}(I) x_{ion} - (M_s/M_m) \sum_{sol,ion} [B_{sol,ion}(I) + IB'_{sol,ion}(I)] \\ &x'_{sol} m_{ion} - M_s \sum [B_{ca}(I) + IB'_{ca}(I)] m_c m_a + \ln x_s \\ &+ \ln(1-\phi_2) - r_1 \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \phi_2 \\ &+ r_1 \left[C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon} \right] \phi_2^2 \\ &- 2r_1 \left[\left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + C_\gamma \tilde{\varepsilon} \right] \phi_2^3 + 3r_1 C_\gamma \tilde{\varepsilon} \phi_2^4 \quad (24) \end{aligned}$$

Group Contribution.

Van der Waals Energy Contribution: The energy parameter ε_{ij}^* in eq. (17) is due to van der Waals forces (dispersion and polar forces). For a pure component i , ε_{ii}^* can be estimated using the square of the pure-component van der Waals solubility parameter of Hansen (Barton),³⁷ which is the sum of a dispersion contribution and a polar contribution: $\delta_{vdw}^2 = \delta_d^2 + \delta_p^2$.

$$\delta_{vdw,i}^2 = \frac{3N_A \varepsilon_{ii}^* r_i}{V_{mi}} \quad (25)$$

where N_A is the Avogadro number and where δ_{vdw}^2 and V_{mi} are at 25 °C. For pure component, the effect of temperature on ε_{ii}^* is given by

$$\varepsilon_{ii}^* = \frac{\varepsilon_{ii}^+}{V_{mi}} \quad (26)$$

where V_{mi} depends on temperature. The temperature-independent parameter ε_{ii}^+ can be estimated by

$$\varepsilon_{ii}^+ = \frac{\delta_{vdw}^2 V_{mi}^2 (25^\circ \text{C})}{3N_A r_i} \quad (27)$$

The cross interaction van der Waals energy parameter ε_{ij}^* is estimated by the geometric mean of the corresponding

pure-component parameters

$$\varepsilon_{ij}^* = \sqrt{\varepsilon_{ii}^* \varepsilon_{jj}^*} \quad (28)$$

Specific Energy Contribution: The pure-component parameters $\delta\varepsilon_{ii}$ and $\delta\varepsilon_{jj}$ are calculated from Hansen's hydrogen bonding solubility parameter δ_h . It is related to the additional specific energy $\Delta U_{sec,ii}$ by

$$\Delta U_{sec,ii}(25^\circ\text{C}) = -\delta_h^2 V_{mi}(25^\circ\text{C}) \quad (29)$$

For the temperature dependence of $\Delta U_{sec,ii}$, we assume

$$\Delta U_{sec,ii} = \frac{\Delta U_{sec,ii}^+}{V_{mi}} \quad (30)$$

where $\Delta U_{sec,ii}^+$ is independent of temperature. From eqs. (15) and (16), we get

$$\Delta U_{sec,ii}(T) = \frac{\delta_h^2 V_{mi}^2(25^\circ\text{C})}{V_{mi}(T)} \quad (31)$$

For a pure component i , upon inserting eq. (5) into the thermodynamic relation $\left[\frac{\partial(\Delta A/T)}{\partial(1/T)}\right] = \Delta U$, we have

$$\frac{\Delta U_{sec,ii}}{k} = \frac{N_s r_i z C_\alpha (1-\eta) \eta \left(\frac{\delta\varepsilon_{ii}}{k}\right)}{\left[1 + C_\alpha \frac{\delta\varepsilon_{ii}}{kT} (1-\eta) \eta\right]^2} \quad (32)$$

Cross specific energy parameter $\delta\varepsilon_{ij}$ is calculated from pair-interaction group parameters

$$\frac{\delta\varepsilon_{ij}}{k} = \sum_{m=1}^{N_s} \sum_{n=1}^{N_p} \phi_m \phi_n g_{mn} \quad (33)$$

where N_s and N_p are number of groups in solvents and polymers, respectively. ϕ_m and ϕ_n are volume fractions of group m in a solvent and that of group n in a polymer, respectively; g_{mn} are pair interaction parameters between group m in a solvent and group n in a polymer. To improve the accuracy of prediction, we assume that a functional group in a polymer is different from that in a solvent.

In this study, they are estimated by fitting experimental vapor-liquid equilibria data of non-electrolyte polymer solutions³⁸ and perfluoro-sulfonated polymer electrolyte membranes/water.³⁵

Results and Discussion

We proposed a new group-contribution model to describe the vapor-liquid equilibria for a variety of polymer/solvent systems. The new model employs the secondary lattice concept to take into account an oriented interaction. The advantage of this model follows from its simplicity. In this work, most parameters are calculated from pure-component properties, either from experimental data or from published esti-

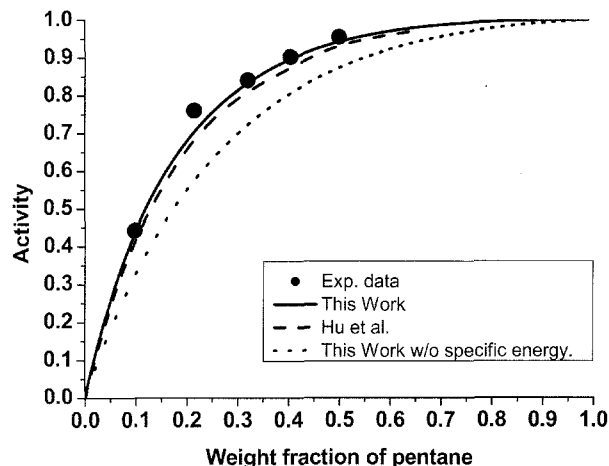


Figure 1. Solvent activities for the PIB (polyisobutylene, $M_w = 1,170$)/pentane system at 298.15 K. The dark circles are experimental data by Wen *et al.*³⁸

mation methods. To establish the group-contribution method, the most significant role is to determine the cross-pair interaction between polymer and solvent segments.

Non-Electrolyte Polymer/Solvent Mixture Systems.

Figure 1 shows a comparison with activities of PIB ($M_w = 1,170$)/pentane system at 298.15 K calculated by Hu *et al.*¹⁶ and with that of this work. The solid line is calculated by this work, the dashed line is from Hu *et al.*¹⁶ and the dotted line is from this work without specific energy. Dark circles are experimental data reported by Wen *et al.*³⁸ Both models give fairly good agreement with experimental results. However, Hu *et al.*'s Model needs 18 group parameters and the proposed model requires only 6 parameters. When result calculated from the proposed model without specific energy is compared with experimental data, it differs from experimental data. Calculated group parameters from Hu *et al.*'s model are listed in Table I and all parameters from this work are listed in Table II.

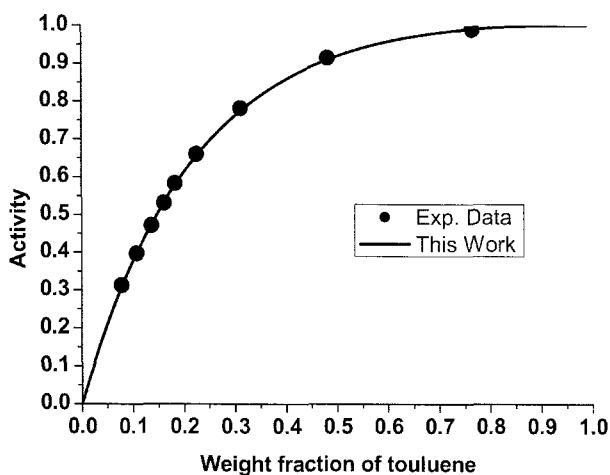
The solid line is calculated by this work. Dark circles are experimental data reported by Wen *et al.*³⁸ Selecting molar volumes at different temperatures for pure component i , ε_{ii}^* , ε_{ij}^* , $\delta\varepsilon_{ii}$, and $\delta\varepsilon_{ij}$ are calculated. The pair interaction

Table I. Group-Interaction Parameters by Hu *et al.*¹³

Solvent	Polymer			
	CH ₃	CH ₂	C	
CH ₃	$g_{mn}(1)$	81.6	-71.8	1956.6
	$g_{mn}(2)$	-	-669.5	-
	$g_{mn}(3)$	-	2439.9	-8909.2
CH ₂	$g_{mn}(1)$	-	663.3	-2115.6
	$g_{mn}(2)$	-	-1088.5	-
	$g_{mn}(3)$	1614.5	-	-9250.0

Table II. Group-Interaction Parameters: $g_{mn}(K)$

Solvent	Polymer					
	CH ₃	CH ₂	CH	C	C ₆ H ₅	O
CH ₃	2980.1	-2493.9	-1761.2	-5486.5	-586.0	-
CH ₂	1512.1	-6960.2	-	-5219.4	-	-
C ₆ H ₅	-	769.9	-3017.3	-	194.4	2845.6
H	-	-5776.1	-	-	-	1434.7
OH	-	-1598.9	-	-	-	-1190.5

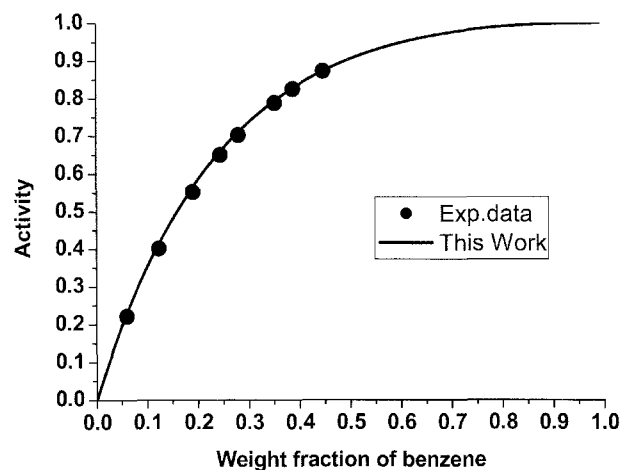
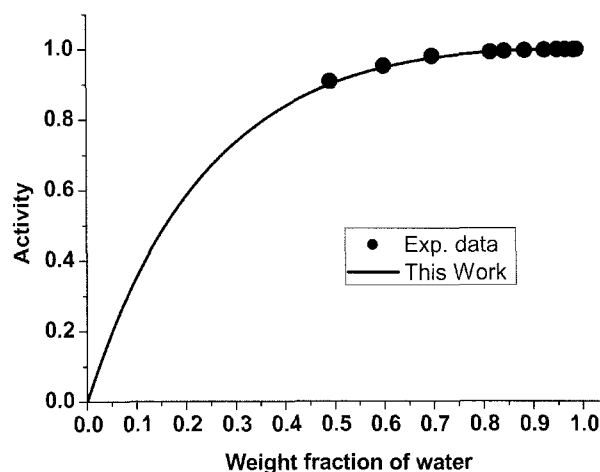

Figure 2. Solvent activities for the PS (polystyrene, $M_w=10,920$)/toluene system at 321.65 K. The dark circles are experimental data by Wen *et al.*³⁸

energy parameter values are $g_{CH_3-CH_3} = 2980.016$ K, $g_{CH_2-CH_3} = -2493.92$ K, $g_{C-CH_3} = -5486.497$ K, $g_{CH_3-CH_2} = 1512.1428$ K, $g_{CH_2-CH_2} = -6960.18$ K, and $g_{C-CH_2} = -5219.42$ K. Selecting molar volumes at different temperatures for pure component i , $\delta\varepsilon_i$ can be calculated from eq. (28). The pair interaction energy parameter values are obtained by fitting the experimental data at 298.15 K.

Figure 2 shows described solvent activities of poly(styrene) (PS, $M_w = 10,920$)/toluene systems at 321.65 K. The solid line is calculated by this work. Dark circles are experimental data reported by Wen *et al.*³⁸ The pair interaction energy parameter values are $g_{CH_2-CH_3} = -2493.92$ K, $g_{CH-CH_3} = -1761.21$ K, $g_{C_6H_5-CH_3} = -586.017$ K, $g_{CH_2-C_6H_5} = 769.864$ K, $g_{CH-C_6H_5} = -3017.28$ K, and $g_{C_6H_5-C_6H_5} = 194.429$ K. As shown in this figure, the calculated curve agrees very well with experimental data.

Figure 3 shows described solvent activities of poly(ethylene oxide)(PEO, $M_w = 100,000$)/benzene system at 343.15 K. The solid line is predicted by this work. Dark circles are experimental data reported by Wen *et al.*³⁸ The pair interaction energy parameter values are $g_{CH_2-C_6H_5} = 769.864$ K, $g_{O-C_6H_5} = 2845.58$ K, $g_{CH_2-H} = -5776.11$ K, and $g_{O-H} = 1494.65$ K.

Figure 4 shows predicted solvent activities of poly(ethylene


Figure 3. Solvent activities for the PEO (poly(ethylene oxide), $M_w=100,000$)/benzene system at 343.15 K. The dark circles are experimental data by Wen *et al.*³⁸

Figure 4. Solvent activities for the PS (polystyrene, $M_w=1,460$)/water system at 273.15 K. The dark circles are experimental data by Wen *et al.*³⁸

oxide) (PEO, $M_w = 1,460$)/water system at 273.15 K. The solid line is calculated by this work. Open circles are experimental data reported by Wen *et al.*³⁸ The pair interaction energy parameter values are $g_{CH_2-H} = -773.512$ K, $g_{O-H} = -1635.89$ K, $g_{CH_2-OH} = -1598.88$ K, and $g_{O-OH} = -1190.52$ K. In this case,

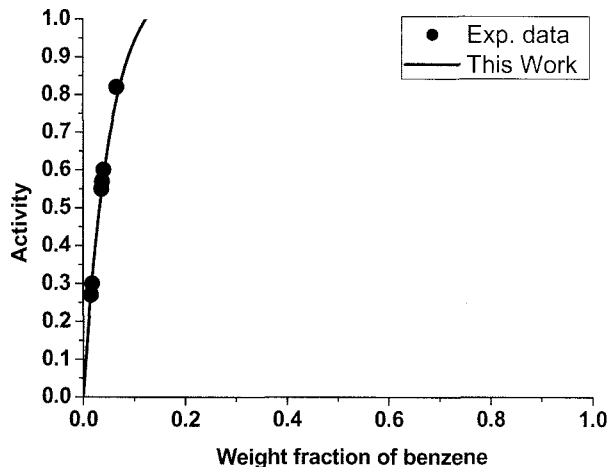


Figure 5. Solvent activities for the PE (polyethylene, $M_w=80,000$)/benzene system at 273.15 K. The dark circles are experimental data by Wen *et al.*³⁸

agreement with experimental data shows slight deviation compared with other results. The proposed model does not consider the various polydispersity of chain molecules. Particularly, poly(ethylene oxide) has a high polydispersity number ($M_w/M_n = 1.6$), this model implicitly assumes that all the polymers are monodisperse. It is likely that this deficiency is responsible for the observed discrepancy between the proposed model and experimental data.

Figure 5 shows described solvent activities of poly(ethylene) (PE, $M_w = 80,000$)/benzene system at 273.15 K. The solid line is predicted by this work. This result is predicted by using only previously obtained pair interaction energy parameters. Open circles are experimental data reported by Wen *et al.*³⁸ The pair interaction energy parameter values are $g_{CH_2-C_6H_5} = 769.864$ K, and $g_{CH_2-H} = -5776.11$ K. These parameters are not obtained by fitting experimental data.

Perfluoro-Sulfonated Polymer Electrolyte Membranes/Water System. We propose the g^E group-contribution model to predict water activities of perfluorosulfonic acid polymer electrolyte systems. We employ the chain length dependence of the high molecular weight distribution to extend the previous model¹⁹ to polymer/solvent systems. Our proposed model has two kinds of adjustable model parameters: middle-range parameters (b_{ij} , c_{ij}) and short-range parameter (g_{ij}).

Figure 6 shows basic structures of Nafion, Aciplex and Flemion. Figure 7 compares calculated water activities of Nafion 125 (duPont, EW=1,200) with experimental data reported by Hinatsu *et al.*³⁵ Model interaction parameter values are $b_{H_2O-SO_3^-} = 0.818$, $b_{H_2O-H^+} = 0.818$, $b_{SO_3^- - H^+} = 1.131$, $c_{H_2O-SO_3^-} = -3.768$, $c_{H_2O-H^+} = -3.768$, $c_{SO_3^- - H^+} = 18.162$, $g_{CF-H_2O} = 4470.82$, $g_{CF_2-H_2O} = 344.832$, $g_{CF_3-H_2O} = 3866.79$, $g_{O-H_2O} = 7947.35$. These parameter values are obtained using only Nafion125/water system. As shown in this figure, the calculated curve agrees well with experimental data. All parameters are listed in Tables III and IV.

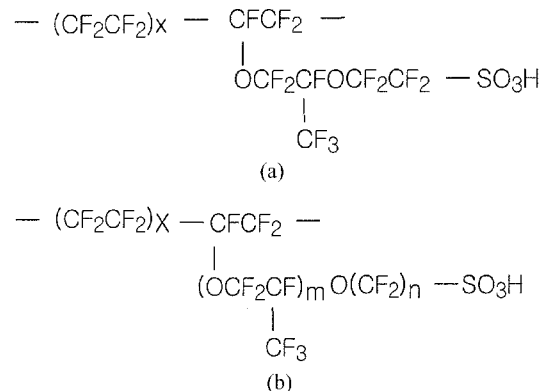


Figure 6. Repeat unit structures structures of perfluorinated proton exchange membrane with sulfonic acid functional groups. (a) Nafion ($x = 5-11$) and (b) Aciplex and Flemion ($m=0$ or 1 , $n=2-5$, $x=1.5-14$).

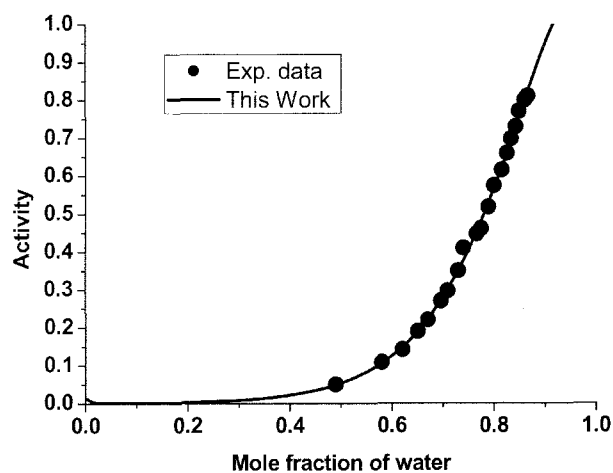


Figure 7. Solvent activities for the Nafion (E.I. DuPont de Nemours and Company)/water system at 353.15 K. Nafion 125 (EW=1,200). Dark circles are experimental data by Hinatsu *et al.*²²

Table III. Middle-Range Interaction Parameters; b_{ij} , c_{ij}

i	j	b_{ij}	c_{ij}
H ₂ O	SO ₃ ⁻	0.8	-3.8
H ₂ O	H ⁺	0.8	-3.8
SO ₃ ⁻	H ⁺	1.1	18.2

Table IV. Short-Range Interaction Parameters; g_{ij}

i	j	g_{ij}
CF	H ₂ O	4470.8
CF ₂		344.8
CF ₃		3866.8
O		7947.4

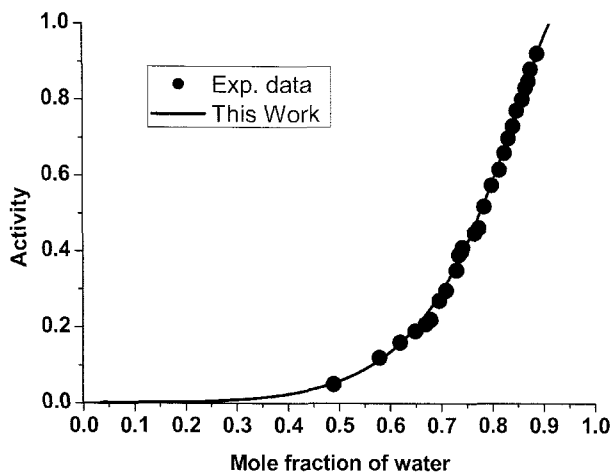


Figure 8. Solvent activities for the Nafion (E.I. DuPont de Nemours and Company)/water system at 353.15 K. Nafion 117 (EW=1,100). Dark circles are experimental data by Hinatsu *et al.*²²

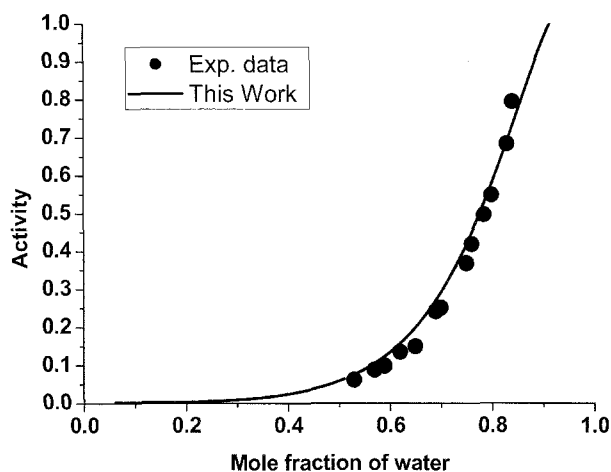


Figure 10. Solvent activities for the Aciplex (Asahi Chemical Industry Co.)/water system at 353.15 K. Aciplex 12 (EW=1,080). Dark circles are experimental data by Hinatsu *et al.*²²

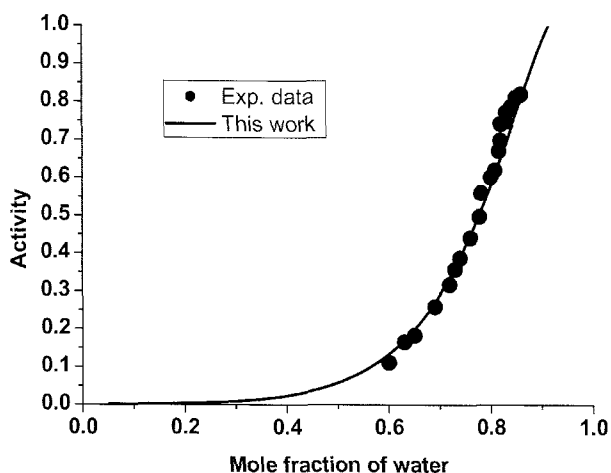


Figure 9. Solvent activities for the Flemion (Asahi Glass)/water system at 353.15 K. Flemion4 (EW=890). Dark circles are experimental data by Hinatsu *et al.*²²

Figures 8, 9 and 10 represent water activities of and Nafion 117 (duPont, EW=1,100), Flemion (Asahai Glass, EW=890) and Aciplex (Asahai Chemical, EW=1,080). Solid lines are calculated by using previously obtained model interaction parameters with no additional adjustable model parameters. Dark circles are experimental data reported by Hinatsu *et al.*³⁵

The ultimate goal of the group-contribution model lies in its ability to predict physical properties for systems which are not included in the experimental data, that is, the set of data uses to determine the parameters. The proposed model agrees still very well with the experimental data using previously obtained parameters.

In this study, we determined model interaction parameters between polymer and solvent groups.

More group parameters are required to cover most com-

mon non-electrolyte polymer/solvent systems and much more experimental data is needed in order to calculate group parameters of electrolyte polymer/solvent systems. We considered polymer solutions at temperature well below the solvent's critical temperature. We expect that the free volume effect as described by Patterson³⁹ is almost negligible in our proposed model systems. Also, various flexibilities of chain molecules and polydispersities are not considered in this study. The model implicitly assumes that polymer has the same flexibility and monodispersity. Furthermore, solvent molecules are considered to be monomers where the concept of flexibility does not apply.

Conclusions

We proposed a group-contribution model based on a modified double lattice theory. The proposed model includes the long range interaction and middle range interaction from charge effects and the short-range interaction is covered form modified double lattice model. The proposed model has a simplified and improved expression for the Helmholtz energy of mixing for polymer/solvent systems that includes the combinatorial entropy contribution, the van der Waals energy contribution and the specific energy contribution. Pair interaction parameter which is calculated by group contribution method helps to understand what type of pair group parameter influences experimental results. We showed several solvent activities of various binary polymer/solvent systems comparing calculated results with experimental data. The proposed model gives very good agreement with experimental data.

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